Hollow Ag/carbon microporous spheres with high catalytic activity based on a bio-inspiration polydopamine reaction platform†

Qian Zhang,[ab] Chen Zhou[a] and Aisheng Huang[*a]

Based on a bio-inspiration polydopamine reaction platform, hollow Ag/carbon microporous spheres were facilely prepared through a template-assisted method. The hollow Ag/carbon spheres, with a uniform shell thickness of 30 nm and a high Ag loading, show high catalytic activity for the reduction of 4-nitrophenol by NaBH$_4$ to 4-aminophenol. It is found that the 4-nitrophenol (10 mL, 1×10^{-3} M) can be completely converted to 4-aminophenol in 2 min by adding 20 mg of hollow Ag/carbon catalysts. The catalytic activity of the hollow Ag/carbon microporous spheres is also confirmed by CO oxidation. At 200 °C, 100% CO conversions can be achieved by using hollow Ag/carbon microporous spheres as catalysts, which is promising to replace other noble metal catalysts in metal catalyzed reactions.

Introduction

Supported metal nanoparticles are widely used as heterogeneous catalysts in chemical industries.[1,2] The surface of the metal nanoparticles is the catalytic site where the reactants can be adsorbed and converted to products. Therefore, not only the size, shape, and composition of the metal nanoparticles, but also the shape, composition, and microstructure of the catalyst supports play an important role in determining the overall catalytic activity and the product selectivity.[3,4] So far, various materials including metal oxides,[5–7] silica,[8] and carbon,[9–11] have been developed as catalyst supports. Among these catalyst supports, hollow carbon nanospheres (HCSs) have drawn considerable interest due to their high thermal and chemical stability, high surface-to-volume ratio, low density, excellent corrosion resistance, and easy chemical processing.[12–14] Several strategies such as chemical vapor deposition,[15] hydrothermal treatment,[16] and template-assisted method[17,18] were developed for the preparation of hollow carbon nanospheres. Template-assisted is the main method used to prepare hollow carbon spheres. Generally, a spherical core–shell structure is firstly formed through the deposition of carbon precursor on a hard template core, followed by carbonization at high temperature and then core removal to obtain hollow carbon spheres. It is

well known that the carbon precursors have an important effect on the preparation and final physical and chemical properties of the resulting hollow carbon nanospheres.[19] Besides a high carbon yield, the formation of thin and uniform carbon layer has to be considered in the template synthesis of hollow carbon nanospheres since a thin and uniform carbon layer is helpful to promote the facile and fast diffusion of the chemicals, thus resulting in a high catalytic activity of the catalysis.[17] Therefore, it is high desired to develop a simple and powerful method to prepare thin and uniform carbon shell on the template core.

Mussel adhesive protein excreted by marine mussel has attracted much attention because of its outstanding adhesion ability to almost all substrates.[20] Inspired by the bioadhesion property of mussels, Messersmith and co-workers reported that dopamine (DPA) could polymerize to polydopamine (PDA), and stick to all kinds of organic and inorganic surfaces.[21] The PDA has emerged as a versatile and powerful platform of secondary reaction for application in cells adhesion, proteins immobilization
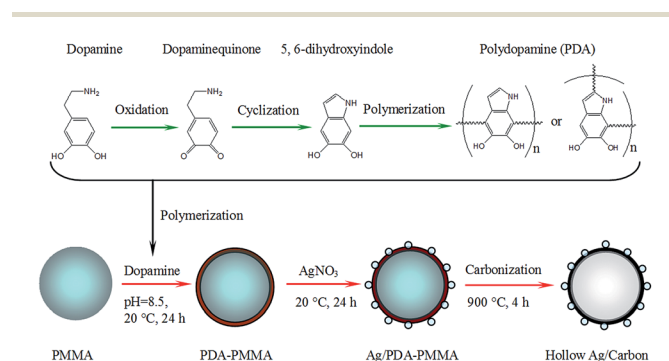
[a]Institute of New Energy Technology, Ningbo Institute of Material Technology and Engineering, CAS, 1219 Zhongguan Road, 315201 Ningbo, P. R. China. E-mail: huangaisheng@nimte.ac.cn

[b]Nano Science and Technology Institute, University of Science and Technology of China, 166 Renai Road, 215123 Suzhou, P. R. China

Fig. 1 Schematic diagram of the preparation of hollow Ag/carbon spheres based on bio-inspiration polydopamine reaction platform.

nanoparticles stabilization, and membranes preparation.[22–27] Attributing to its adhesive ability through non-covalent adsorption and covalent reaction, PDA is very promising to be used as a carbon source to deposit on the template core for the preparation of thin and uniform hollow carbon spheres.[17] Further, the PDA is an extremely versatile platform for facile introduction of dispersive and adherent metal nanoparticles by electroless metallization.[28] In the present work, we report the preparation of hollow Ag/carbon microporous spheres based on the PDA reaction platform (Fig. 1). The catalytic activity of the hollow Ag/carbon catalysts is evaluated by the reduction of 4-nitrophenol and CO oxidation.

Experimental

Materials

Chemicals were used as received: 2,2′-azobis(2-methyl-propionamidine)dihydrochloride (97%, Aldrich), methyl methacrylate (MMA, 97%, Aldrich), dopamine (98%, Aladdin), tris(hydroxymethyl)aminomethane (Tris–HCl, 99%, Aladdin), silver nitrate (AR, Aladdin), ethanol (98%, Aladdin), 4-nitrophenol (≥99.0%, Aladdin), sodium borohydride (NaBH$_4$, 98%, Aladdin), doubly distilled water.

Preparation of polymethyl methacrylate (PMMA) spheres

Mono-disperse PMMA spheres were synthesized according to the procedure reported elsewhere.[29] 1500 mL of water and 400 mL of MMA were added into a three-neck round-bottom flask which was purged with nitrogen. The mixture was heated to 75 °C with continued stirring. When the temperature kept constant, 1.5 g 2,2′-azobis(2-methylpropionamidine)dihydrochloride was added as azo initiator to the above mixture, and then the reaction was continued for 2 h to produce colloidal PMMA spheres. The PMMA spheres were obtained by centrifuging, filtrating and drying the colloidal PMMA. Before being used as templates, the PMMA crystal pellets were crushed with a metal spatula to form a powder.

DPA modification of PMMA spheres

Simple immersion of PMMA spheres (0.3 g) in a dilute aqueous solution of dopamine (30 mL) in air at a typical pH of marine environment (pH = 8.5), with constant agitation for 24 h at 20 °C. Dopamine can self-polymerize to polydopamine at an alkaline environment, resulting in polydopamine layer being deposited on the support surface of PMMA spheres.[21,25] And then, the PDA-modified PMMA spheres were obtained by filtrating and washing with deionized water, and then drying at a low temperature (<50 °C).

Preparation of hollow Ag/carbon microporous spheres

Afterwards, the PDA-modified PMMA spheres were treated with AgNO$_3$ solution (0.1 mol L^{-1}) for 24 h at 20 °C. After filtrating and washing with ethanol for several times, Ag/PDA-PMMA spheres were dried at a low temperature (<50 °C). Finally, carbonization was carried out under Ar atmosphere at 900 °C

for 4 h with a heating rate of 3 °C min^{-1} to prepare hollow Ag/carbon microporous spheres.

For comparison, Ag catalysts were also supported on the surface of PDA-modified carbon nanotubes (CNTs) and PDA-modified carbon black (CB) prepared with same method under same synthesis condition with Ag/carbon.

Characterization of hollow Ag/carbon microporous spheres

Field emission scanning electron microscope (FESEM) micrographs were taken on an S-4800 (Hitachi) with a cold field emission gun operating at 4 kV and 10 μA. The chemical composition of the Ag/PDA-PMMA spheres and hollow Ag/carbon spheres were characterized by energy-dispersive X-ray spectroscopy (EDXS) using the same SEM microscope at 20 kV and 20 μA. The surface chemical compositions of the Ag/PDA-PMMA spheres and hollow Ag/carbon spheres analyzed by X-ray photoelectron spectroscopy (XPS, Axis Ultra DLD, Kratos) with Mg Kα lines as an X-ray source. The XRD patterns were recorded at 20 °C under ambient conditions with Bruker D8 ADVANCE X-ray diffractometer with CuKα radiation at 40 kV and 40 mA. Textural properties of Ag/PDA-PMMA spheres and hollow Ag/carbon spheres, including Brunauer–Emmett–Teller (BET)-specific surface areas, and pore volumes were analyzed by nitrogen adsorption/desorption isotherm data measured on an ASAP 2020M apparatus (at 77.3 K).

Catalytic activity evaluation of the hollow Ag/carbon microporous spheres

The silver-catalyzed reduction of 4-nitrophenol by NaBH$_4$ to 4-aminophenol was chosen as a model reaction to evaluate the catalytic ability of the as-synthesized hollow Ag/carbon microporous spheres. 10 mL (1 × 10^{-3} mol L^{-1}) 4-nitrophenol was mixed with freshly prepared aqueous solution of NaBH$_4$ (0.1 mL, 1 × 10^{-1} mol L^{-1}). And then, 20 mg Ag/carbon spheres were added with constant magnetic stirring of 300 rpm. UV/Vis absorption spectras were recorded to monitor the change in the reaction mixture. The conversion of 4-nitrophenol is defined as the percentage of 4-nitrophenol concentration that has reacted.

$$\alpha(\%) = \frac{C_{\text{initial}} - C_{\text{final}}}{C_{\text{initial}}} \times 100\%$$

C_{initial} is the 4-nitrophenol concentration before reduction and C_{final} is the 4-nitrophenol concentration after the addition of the hollow Ag/carbon catalyst in 2 min. The 4-nitropheno concentration was determined by UV/Vis according to the Lambert–Beer law.

The catalytic activity of the hollow Ag/carbon microporous spheres was also confirmed by CO oxidation. For comparison, the catalytic activity of the Ag/CNTs and Ag/CB was also evaluated by CO oxidation. The CO oxidation was evaluated on a Finesorb 3010 instrument with a fixed-bed U-shaped quartz reactor with 3 mm internal diameter.[30] 20 mg of Ag/carbon catalysts were used for each test, and the reaction temperature with a heating rate of 2 °C min^{-1} was controlled by using a K-type thermocouple which directly contacted with the upper

quartz wool near the Ag/carbon powder (Fig. S1†). The composition of the feed gas included 2% CO and 98% air (as the balance gas), and the total feed flow rate was 30 mL min^{-1}. The effluent gas was analyzed by using an FGA-4100 which was equipped with infrared sensor to detect CO, CO_2 and O_2. The conversion of CO is defined as the percentage of CO feed that has reacted:

$$CO(\%) = \frac{CO_{in} - CO_{out}}{CO_{in}} \times 100\%$$

CO_{in} is the CO concentration in the inlet gas and CO_{out} is the CO concentration in the outlet gas.

Results and discussion

As shown in Fig. 2a, the as-synthesized PMMA spheres show a smooth surface and a uniform size with a diameter of about 320 nm. After PDA modification, the diameter of the PMMA spheres enlarges to about 400 nm, and the surface of PDA-PMMA becomes much rougher (Fig. 2b), suggesting that DPA can spontaneously self-assemble into PDA and deposit onto the surface of PMMA spheres. Furthermore, it can be learned that the thickness of the PDA layer is about 40 nm, which is in good agreement with the previous report.[21] Further, the metal-binding ability of catechols presented in the PDA coating is expected to deposit adherent and uniform metal nanoparticles onto substrates surface by electroless metallization. This is demonstrated through the deposition of silver nanoparticles onto the surface of PMMA spheres via simple immersion of PDA-modified PMMA spheres into silver nitrate solution. As shown in Fig. 2c, after reaction with Ag$^+$ in $AgNO_3$ solution, silver nanoparticles are scattered on the PDA-PMMA surface. It is observed that Ag nanoparticles with about 10 nm appear as brighter spots on the PDA-PMMA surface (the inset in Fig. 2c). The formation of Ag nanoparticles on the PDA-PMMA surface is

Element	Wt %	At %
C	71.46	82.81
N	4.97	4.94
O	12.43	10.81
Ag	11.15	1.44

Element	Wt %	At %
C	58.36	87.24
N	2.42	3.10
O	3.28	3.68
Ag	35.93	5.98

Fig. 3 EDXS of the Ag/PDA-PMMA spheres (a) and hollow Ag/carbon spheres (b).
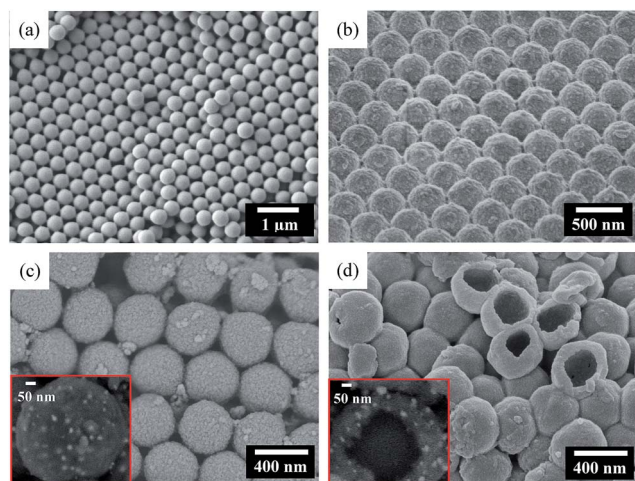
Fig. 2 FESEM images of the PMMA spheres (a), PDA-modified PMMA spheres (b), Ag/PDA-PMMA spheres (c), hollow Ag/carbon spheres (d). The inset in (c) shows a magnified image of an Ag/PDA-PMMA sphere, and the inset in (d) shows a magnified image of a hollow Ag/carbon sphere.
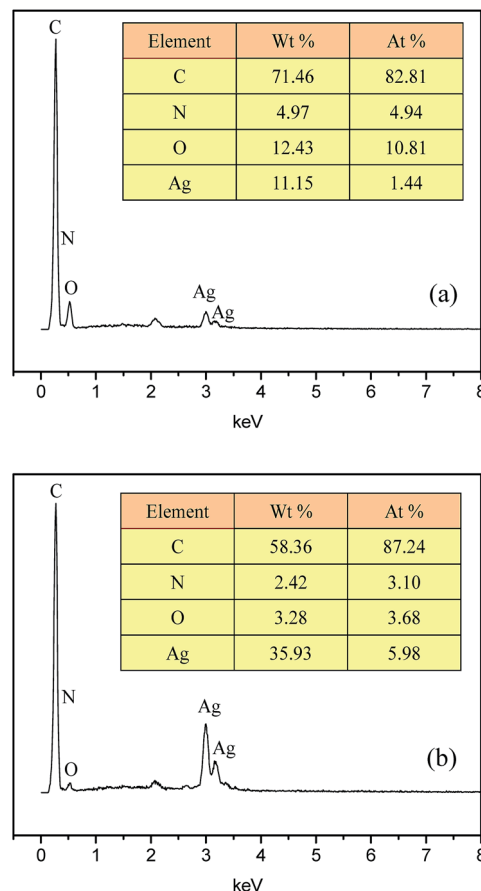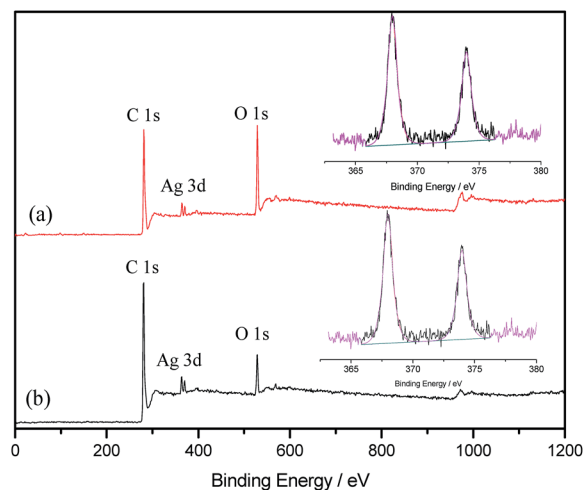
Fig. 4 XPS of the Ag/PDA-PMMA spheres (a) and hollow Ag/carbon spheres (b). The insets show corresponding narrow scan for Ag 3d peaks.

also confirmed by EDXS (Fig. 3a), XPS (Fig. 4a) and XRD pattern (Fig. S2a†). The peaks in XRD pattern at 38.1°, 44.2°, 64.5°, and 77.5° correspond to the (111), (200), (220), and (311) diffractions of metallic Ag.[28]

At 900 °C, the PMMA templates are easily removed, resulting in the formation of hollow Ag/carbon spheres with diameter of about 400 nm (Fig. 2d). The hollow nanostructure is also observed by TEM image of the Ag/carbon spheres (Fig. S3†), showing a clear shell with thickness of about 30 nm, which is comparable to the thickness of the PDA layer (about 40 nm). The Ag nanoparticles are highly dispersed on the surface of hollow carbon spheres (the inset in Fig. 2d). Furthermore, EDXS indicates the high purity of the carbon and silver composition with only a small number of other elements (Fig. 3b). In addition, the structure of metallic Ag keeps unchanged after carbonization at a high temperature, as confirmed by XPS (Fig. 4b) and XRD (Fig. S2b†). Nitrogen adsorption–desorption isotherm of the Ag/carbon spheres shows a typical type-I curve, confirming a microporous structure of the hollow Ag/carbon spheres (Fig. S4†). The BET surface area of the hollow Ag/carbon spheres is 242 m^2 g^{-1}, which is much higher than that of Ag/PDA-PMMA spheres (4.24 m^2 g^{-1}). Considering the high BET area and highly porous structure, the hollow Ag/carbon spheres can be used as an excellent catalyst.

The catalytic ability of the hollow Ag/carbon spheres was evaluated with the reduction of 4-nitrophenol by $NaBH_4$ to 4-aminophenol. The reduction reaction can't start in the absence of hollow Ag/carbon catalyst. The bright yellow colour of the 4-nitrophenol and $NaBH_4$ mixture keeps unchanged for at least 5 days at 20 °C (Fig. S5a†), and a strong and constant absorption peak of 4-nitrophenol is observed at 400 nm (Fig. 5). However, when hollow Ag/carbon catalyst was added into the 4-nitrophenol and $NaBH_4$ solution, the solution colour become weaker and weaker, and finally become colourless in 2 min (Fig. S5b and a video in ESI†), indicating that the 4-nitrophenol is completely converted to 4-aminophenol. Correspondingly, the absorption at 400 nm quickly decreases and finally disappears, and a new absorption of 4-aminophenol at 295 nm is emerged (Fig. 5).

Dai and colleagues reported the preparation and catalytic ability of Au@carbon yolk–shell nanocomposites.[17] It was found that the Au@carbon yolk–shell nanocomposites showed high catalytic ability in the reduction of 4-nitrophenol, and the reduction of 4-nitrophenol (3 mL, 1×10^{-4} M) into 4-amino-phenol was completely finished in 5 min by using 5 mg Au@carbon. The high catalytic ability of Au@carbon was attributing to a facile diffusion of 4-nitrophenol through the porous and ultrathin carbon shell and the large free reaction voids inside the carbon sphere. In comparison with the Au@carbon yolk–shell nanocomposites, the present hollow Ag/carbon spheres also show high catalytic ability, and only in 2 min the 4-nitrophenol (10 mL, 1×10^{-3} M) can be completely transformed to 4-aminophenol by adding 20 mg hollow Ag/carbon catalysts. As shown in the inset in Fig. 2d, Ag nanoparticles can highly disperse on the surface of hollow carbon, thus leading to the formation of more silver active sites for 4-nitrophenol reduction.

The catalysts stability is a very important factor for catalytic reaction. The stability of hollow Ag/carbon was investigated by performing the same reduction reaction. After each use, the hollow Ag/carbon catalyst was recycled by simple centrifugation, washing with distilled water and drying in an oven overnight. It can be seen that the hollow Ag/carbon catalyst still shows highly active after 6 successive cycles of reactions, with near 100% conversion in 2 min (Fig. S6†), indicating the high stability of the hollow Ag/carbon.

The catalytic oxidation of CO to CO_2 using Ag catalyst at low temperature has attracted considerable interest due to its significance in a wide range of applications.[31,32] The catalytic activity of the hollow Ag/carbon catalyst was also confirmed by the CO oxidation reaction. Fig. 6 shows the CO conversion as a function of the reaction temperature by using Ag nanoparticles as catalysts which were loaded on the hollow carbon spheres, carbon nanotubes (CNTs), and carbon black (CB), respectively. It can be seen that both Ag/CNTs and Ag/CB show low catalytic activity. No CO conversion is observed when the reaction temperature is lower than 100 °C, and the CO conversion begins to increase after the reaction temperature increases to 125 °C. But even the reaction temperature increases to 250 °C, the CO conversions for Ag/CNTs and Ag/CB are only 98.9% and
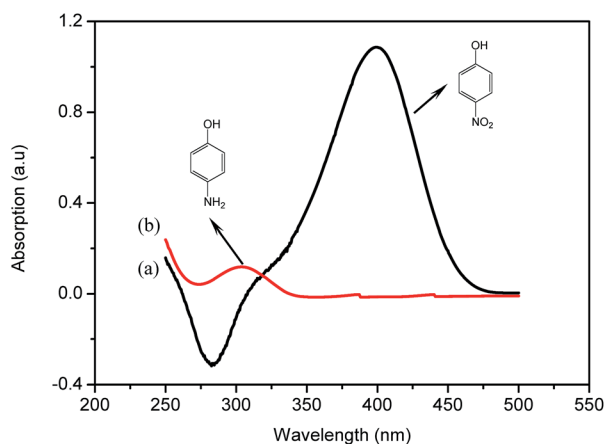

Fig. 5 UV/Vis spectra of 4-nitrophenol solution before reduction (a) and after the addition of the hollow Ag/carbon catalyst in 2 min (b).
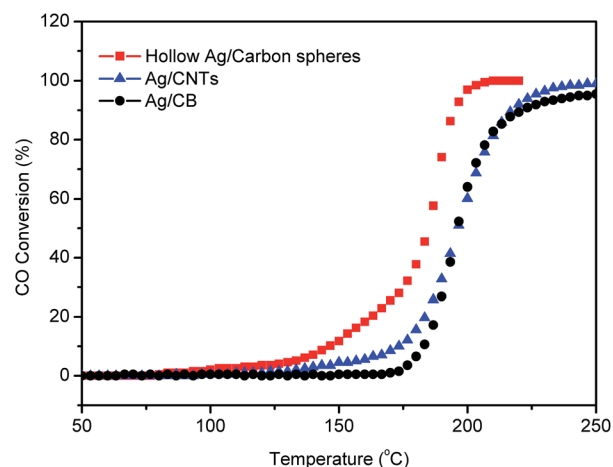

Fig. 6 Temperature-dependent CO conversion in the CO oxidation over the hollow Ag/carbon catalysts. For comparison, the results on the Ag/CNTs and Ag/CB catalysts are also included.

95.4%, respectively. While for hollow Ag/carbon, the CO conversions is about 2% when reaction temperature increases to 100 °C, and 100% CO conversions can be achieved at 200 °C, indicating the hollow Ag/carbon show a higher catalytic activity for CO oxidation than Ag/CNTs and Ag/CB. The characteristic temperatures at the conversion of 10%, 50%, 90%, named as T_{10}, T_{50} and T_{90}, are 146.2 °C, 184.6 °C, 194.8 °C, respectively, showing an excellent activity close to the more expensive Au catalysts.[33] Recently, Nagy *et al.* reported the catalytic performance of SiO_2 supported Ag nanoparticles for CO oxidation.[34] It was found that the maximum CO conversion at 400 °C was only about 90% for Ag/SiO_2. It is well known that the catalyst supports play an important role to the catalytic activity of the catalyst.[35] Since hollow carbon spheres have high BET area, the Ag nanoparticles can be highly dispersed on the surface of hollow carbon, thus showing higher catalytic activity for CO oxidation. Further work is in progress to evaluate catalytic activity of the hollow Ag/carbon for other catalytic reaction.

Conclusions

In conclusion, a versatile and facile method was developed to synthesize hollow Ag/carbon spheres based on polydopamine reaction platform by using PMMA spheres as templates. The uniform Ag/carbon spheres with thin shell thickness of about 30 nm were obtained easily by a simple immersion of the PMMA templates in a dopamine aqueous solution, following the reaction with Ag^+, and finally the carbonization to removal the PMMA templates. The hollow Ag/carbon spheres showed high catalytic ability in the 4-nitrophenol reduction and CO oxidation since Ag nanoparticles can be highly dispersed on the surface of hollow carbon spheres, which is promising to replace other noble metal catalysts in metal catalytic reactions.

Acknowledgements

References

1 A. Corma and H. Garcia, *Chem. Soc. Rev.*, 2008, **37**, 2096.

2 R. J. White, R. Luque, V. L. Budarin, J. H. Clark and D. J. Macquarrie, *Chem. Soc. Rev.*, 2009, **38**, 481.

3 C. K. Tsung, J. N. Kuhn, W. Huang, C. Aliaga, L. Hung, G. A. Somorjai and P. Yang, *J. Am. Chem. Soc.*, 2009, **131**, 5816.

4 K. An, S. Alayoglu, N. Musselwhite, S. Plamthottam, G. Melaet, A. E. Lindeman and G. A. Somorjai, *J. Am. Chem. Soc.*, 2013, **135**, 16689.

5 A. A. Herzing, C. J. Kiely, A. F. Carley, P. Landon and G. J. Hutchings, *Science*, 2008, **321**, 1331.

6 M. M. Schubert, V. Plzak, J. Garche and R. J. Behm, *Catal. Lett.*, 2011, **76**, 143.

7 M. Comotti, W.-C. Li, B. Spliethoff and F. Schüth, *J. Am. Chem. Soc.*, 2006, **128**, 917.

8 M. Okumura, S. Nakamura, S. Tsubota, T. Nakamura, M. Azuma and M. Haruta, *Catal. Lett.*, 1998, **51**, 53.

9 J. Wang, D. Gao, G. Wang, S. Miao, H. Wu, J. Lia and X. Bao, *J. Mater. Chem. A*, 2014, **2**, 20067.

10 S. Ikeda, S. Ishino, T. Harada, N. Okamoto, T. Sakata, H. Mori, S. Kuwabata, T. Torimoto and M. Matsumura, *Angew. Chem., Int. Ed.*, 2006, **45**, 7063.

11 K. T. Lee, Y. S. Jung and S. M. Oh, *J. Am. Chem. Soc.*, 2003, **125**, 5652.

12 C.-H. Hsu, J.-Y. Jan, H.-P. Lin and P.-L. Kuo, *New J. Chem.*, 2014, **38**, 552.

13 F. Xu, Z. Tang, S. Huang, L. Chen, Y. Liang, W. Mai, H. Zhong, R. Fu and D. Wu, *Nat. Commun.*, 2015, **7**, 7221.

14 T. Yang, J. Liu, Y. Zheng, M. J. Monteiro and S. Z. Qiao, *Chem.–Eur. J.*, 2013, **19**, 6942.

15 Z. X. Yang and R. Mokaya, *Microporous Mesoporous Mater.*, 2008, **113**, 378.

16 K. Tang, L. J. Fu, R. J. White, L. H. Yu, M.-M. Titirici, M. Antonietti and J. Maier, *Adv. Energy Mater.*, 2012, **2**, 873.

17 R. Liu, S. M. Mahurin, C. Li, R. R. Unocic, J. C. Idrobo, H. Gao, S. J. Pennycook and S. Dai, *Angew. Chem., Int. Ed.*, 2011, **50**, 6799.

18 G. D. Li, C. L. Guo, C. H. Sun, Z. C. Ju, L. S. Yang, L. Q. Xu and Y. T. Qian, *J. Phys. Chem. C*, 2008, **112**, 189.

19 S. Y. Li, Y. R. Liang, D. C. Wu and R. W. Fu, *Carbon*, 2010, **48**, 839.

20 J. H. Waite and M. L. Tanzer, *Science*, 1981, **212**, 1038.

21 H. Lee, S. H. Dellatore, W. M. Miller and P. H. Messersmith, *Science*, 2007, **318**, 426.

22 H. Lee, J. Rho and P. B. Messersmith, *Adv. Mater.*, 2009, **21**, 431.

23 J. Ryu, S. H. Ku, H. Lee and C. B. Park, *Adv. Funct. Mater.*, 2010, **20**, 2132.

24 D. Ling, W. Park, Y. I. Park, N. Lee, F. Li, C. Song, S.-G. Yang, S. H. Choi, K. Na and T. Hyeon, *Angew. Chem., Int. Ed.*, 2011, **50**, 11360.

25 Q. Liu, N. Wang, J. Caro and A. Huang, *J. Am. Chem. Soc.*, 2013, **135**, 17679.

26 Q. Liu, B. Huang and A. Huang, *J. Mater. Chem. A*, 2013, **1**, 11970.

27 A. Huang, Q. Liu, N. Wang and J. Caro, *J. Mater. Chem. A*, 2014, **2**, 8246.

28 L. Zhang, S. Roy, Y. Chen, E. K. Chua, K. Y. See, X. Hu and M. Liu, *ACS Appl. Mater. Interfaces*, 2014, **6**, 18644.

29 R. C. Schroden, M. Al-Daous, S. Sokolov, B. J. Melde, J. C. Lytle, A. Stein, M. C. Carbajo, J. T. Fernández and E. E. Rodríguez, *J. Mater. Chem.*, 2002, **12**, 3261.

30 C. Zhou, Y. Zhang, L. Hu, H. Yin and W. Wang, *Chem. Eng. Technol.*, 2015, **38**, 291.

31 X. Zhang, Z. Qu, X. Li, M. Wen, X. Quan, D. Ma and J. Wu, *Sep. Purif. Technol.*, 2010, **72**, 395.

32 Z. Qu, M. Cheng, C. Shi and X. Bao, *J. Mol. Catal. A: Chem.*, 2005, **239**, 22.

33 H. H. Kung, M. C. Kung and C. K. Costello, *J. Catal.*, 2003, **216**, 425.

34 G. Nagy, T. BenkÓ, L. BorkÓ, T. Csay, A. Horváth, K. Frey and A. Beck, *React. Kinet., Mech. Catal.*, 2015, **115**, 45.

35 K. Na, S. Alayoglu, R. Ye and G. A. Somorjai, *J. Am. Chem. Soc.*, 2014, **136**, 17207.